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## P. . . ENT COOPERATION TREA . .

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark  
Office  
(Box PCT)  
Crystal Plaza 2  
Washington, DC 20231  
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year)

23 June 1999 (23.06.99)

International application No.

PCT/EP98/07215

Applicant's or agent's file reference

BOR 10 PCT

International filing date (day/month/year)

09 November 1998 (09.11.98)

Priority date (day/month/year)

07 November 1997 (07.11.97)

Applicant

CROZIER, Hérve et al

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

20 May 1999 (20.05.99)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Jean-Marie McAdams

Telephone No.: (41-22) 338.83.38

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

LAINE, Seppo  
SEPPO LAINE OY  
Itämerenkatu 3b  
FI-00180 Helsinki  
FINLANDE

## PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT  
(PCT Rule 71.1)

Date of mailing  
(day/month/year)

08.02.00

Applicant's or agent's file reference  
BOR 10 PCT

### IMPORTANT NOTIFICATION

International application No.  
PCT/EP98/07215

International filing date (day/month/year)  
09/11/1998

Priority date (day/month/year)  
07/11/1997

Applicant  
BOREALIS A/S et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

#### 4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

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D-80298 Munich  
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Authorized officer

Connolly, M

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# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP98/07215

## I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

### Description, pages:

1,2,4,5,7-12, 14-19 as originally filed

3,6,13 as received on 03/12/1999 with letter of 03/12/1999

### Claims, No.:

1-13 as received on 03/12/1999 with letter of 03/12/1999

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**see separate sheet**

4. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims	1-13
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-13
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-13
	No:	Claims	

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP98/07215

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2. Citations and explanations

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**Re Item I**

**Basis of the report**

The applicant has not indicated the passage(s) of the application as filed on which the amendments to operative Claims 3 and 11 are based.

These amendments are considered to contravene Art. 34(2)(b) PCT.

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

D1: EP-A-0 152 701 (cited in the application)

D2: EP-A-0 151 883

D3: GB-A-1 104 665

The claimed subject-matter differs from the teaching of D1 - D3 in that the concentration of the colour pigment is defined.

The prior art documents on file are silent on shrinkage problems associated with pigment-containing propylene polymer compositions.

Therefore, the subject-matter of Claims 1-13 is regarded to meet the requirements of Art. 33 (2)-(4) PCT.

**Re Item VIII**

**Certain observations on the international application**

Claims 3 and 11 are unclear since the conditions under which the shrinkage occurs are not defined (Art. 6 PCT).

Reference is made in this respect to the last par. at p. 13, which refers to a variation in shrinkage in both flow and cross direction of less than 5 % for white, red and blue pigments (compared to conventional, non-nucleated polymers).

The use of vinyl compounds, such as polymers of vinyl cycloalkanes and 3-methyl-1-butene, as nucleating agents in the form of reactor made blends of polypropylene and polymerised vinyl compounds or polypropylene compounds, is suggested in the prior art, cf. EP Patent Specifications Nos. 0 152 701, 0 151 883, 0 368 577 and 0 417 319.

5 However, none of the prior art publications makes any reference to the use of these highly nucleated materials for the production of coloured caps and closures.

According to the present invention it has now surprisingly been found that propylene homo- or copolymers nucleated with a component containing polymerized vinyl compound units will give excellent dimensional consistency by dominating the pigments' nucleating effect with its strong nucleation. The strongly nucleating effect of the polymeric nucleating agent is apparent from the high crystallisation temperature of the polymer. Thus, the crystallisation temperature of the material is at least 7 °C, preferably 10 °C and in particular over 13 °C higher than the crystallisation temperature of the corresponding non-nucleated polymer and the material exhibits a fast crystallisation rate. Caps of various colours moulded with a polypropylene nucleated with a polymerised vinyl compound grade to provide a composition according to the present invention will therefore have practically the same dimensions.

20 More specifically, the polymer composition according to the present invention is characterized by what is stated in the characterizing part of claim 1.

The process according to the present invention for preparing coloured polypropylene compositions is characterized by what is stated in the characterizing part of claim 10.

25 The present compositions can be used in any kind of polymer articles. Particular advantages are obtained by applying the compositions to the manufacture of injection moulded and/or compression moulded products as well as articles produced by thermoforming, blow moulding and film and sheet extrusion.

30 The invention achieves a number of considerable advantages. In particular it should be pointed out that the strong nucleating effect of a polymeric nucleating agent containing

wherein  $R_1$  and  $R_2$  together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

The following specific examples of vinyl compounds can be mentioned: vinyl  
5 cycloalkanes, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl  
cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene, 3-ethyl-  
1-hexene or mixtures thereof. Vinyl cyclohexane (VCH) is a particularly preferred  
monomer but, for example, 3-methyl-1-butene can be used as a monomer or comonomer to  
adjust the crystallisation temperature.

10 For the purpose of the present invention "nucleated propylene polymer" stands for a  
polymer having an increased and controlled degree of crystallinity preferably amounting to  
over 50 % and preferably having a crystallization temperature of more than 7 °C,  
preferably over 10 °C and in particular over 13 °C of the  $T_{cr}$  of the corresponding non-  
15 nucleated polymer. Using  $MgCl_2$ -supported high-yield Ziegler-Natta catalysts  
crystallization temperatures of more than 120 °C, preferably over 124 °C and in particular  
over 126 °C can be obtained. In compositions containing colouring pigments having a  
nucleating effect, particularly advantageous results are obtained by using polymers having  
a crystallization temperature over 15 °C higher than that of the corresponding non-  
20 nucleated polymer (for a polymer produced with the above-mentioned ZN-catalyst, 128  
°C).

According to a preferred embodiment of the present invention, modification of the catalyst  
by polymerizing a vinyl compound, such as VCH, in the presence thereof is performed in  
25 an inert fluid which does not dissolve the polymer formed (e.g. polyVCH). One  
particularly preferred polymerization medium comprises a viscous substance, in the  
following a "wax", such as an oil or a mixture of an oil with a solid or semi-solid polymer  
(oil-grease). The viscosity of such a viscous substance is usually 1,000 to 15,000 cP (1 - 15  
Ns/m<sup>2</sup>) at room temperature. The advantage of wax prepolymerization is that the catalyst  
30 can be prepolymerized, stored and fed into the process in the same media and catalyst wax  
preparation and prepolymerization is performed in the same process device. Due to the  
fact that no washing, drying, sieving and transferring thus are needed, the catalyst activity



high-yield Ziegler-Natta catalysts, having high stiffness, an increased overall degree of crystallization and a crystallization temperature of the propylene homopolymer fraction of more than 120 °C, preferably over 124 °C and in particular over 126 °C. The degree of crystallization for a propylene homopolymer is generally over 48 %, and often over 50 %.

5

The amount of the nucleating polymeric agent is, in case of propylene polymers or copolymers, about 0.0001 to 1 wt-%, and in case of polypropylene blends about 0.0001 to 0.5 wt-%.

10 This nucleated polypropylene (100 parts by weight) is blended with 0.01 to 5 parts by weight of the coloured pigment of choice. The particle size of the pigment is usually 0.01 to 1000 micrometre and more often 0.1 to 10 micrometre.

15 The colouring agent is usually in the form of a masterbatch comprising also a polymer carrier. The blending with the polypropylene is directly done at the conversion machine (e.g. extruder, injection moulding machine...) by dosing the pigment with a gravimetric side feeder. When the colouring agent is liquid it is dosed with a liquid pump.

20 The present polymers and copolymers of propylene can be blended and optionally compounded with additives and adjuvants conventionally used in the art. Thus, suitable additives include antistatic agents, flame retardants, light and heat stabilizers, reinforcement agents, pigments and carbon black. Fillers such as mica, CaCO<sub>3</sub>, talc and wollastonite can also be used. Further, the polymers and copolymers can be blended with non-nucleated propylene and/or with other polymers, in particular other polyolefins, such as LD-, LLD-, MD- and HD-polyethylenes and polybutylene.

25

30 Compositions according to the invention containing pigments will exhibit very small variation in shrinkage irrespective of the colouring agent used. As the results indicated below in Table 1 show, the variation in shrinkage in both flow and cross direction is less than 5 % for white, red and blue pigments compared to conventional, non-nucleated polymers having a variation of shrinkage in the range of 10 to 20 %. The fact that the pigments' nucleating effect is clearly dominated by the nucleated polypropylene with its

## IN THE CLAIMS:

## 1. Coloured polymer composition comprising

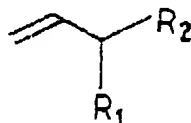
- a propylene polymer nucleated with a polymerized vinyl compound and having an at  
5 least 7 °C higher crystallization temperature than that of the corresponding non-nucleated polymer, and
- a colour pigment having a concentration of 0.01 to 5 wt-% calculated from the weight of the nucleated propylene polymer.

10 2. The composition according to claim 1, wherein the colour pigment has a nucleating effect on the propylene polymer.

3. The composition of claim 1 or 2, wherein the shrinkage of the composition, calculated by comparing the measured dimension of an injection moulded box with the nominal  
15 mould dimension, varies less than 5 % for different colour pigments.

4. The polymer composition according to claim 1, wherein the propylene polymer contains about 0.0001 to 1 % by weight of units derived from a vinyl compound of the formula

20



25 wherein R<sub>1</sub> and R<sub>2</sub> together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

5. The polymer composition according to claim 4, wherein the propylene polymer contains cycloalkane units, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene or  
30 3-ethyl-hexene units or mixtures thereof.

6. The polymer composition according to any of claims 1 to 5, wherein the nucleated

propylene polymer comprises a propylene polymer copolymer polymerized in the presence of a catalyst modified with a polymer containing vinyl compound units.

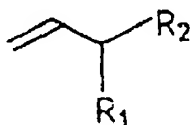
7. The polymer composition according to any of claims 1 to 5, wherein the nucleated propylene polymer comprises a propylene homo- or copolymer blended with a polymer containing polymerised vinyl compound units.

8. The polymer composition according to any of the preceding claims, wherein the pigment is selected from the group of white pigments, yellow/orange pigments, red/violet pigments, blue/green pigments and carbon black.

9. The polymer composition according to claim 8, wherein the pigment is selected from the group of titanium dioxide, isoindolinone, azocondensation, quinacridone, diketo pyrrole pyrrol, ultramarine blue, Cu Phtalocyanine blue and carbon black.

10. A process for preparing a coloured polymer composition comprising a propylene polymer and a colour pigment, characterized by using a propylene polymer nucleated with a polymerized vinyl compound and having an at least 7 °C higher crystallization temperature than the corresponding non-nucleated polymer, the concentration of the colouring pigment being 0.01 to 5 wt-% calculated from the weight of the nucleated propylene polymer,.

11. The process according to claim 10 wherein 100 parts by weight of a nucleated polypropylene composition containing about 0.0001 to 1 % by weight of units derived from a vinyl compound of the formula



wherein R<sub>1</sub> and R<sub>2</sub> together form a 5 or 6 membered saturated or unsaturated or aromatic

ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms is blended with 0.01 to 5 parts by weight of a colouring pigment selected from the group of white pigments, green pigments, red pigments, blue pigments and carbon black, to provide a coloured polypropylene composition, the shrinkage of which varies less than 5 % for different colour pigments, said shrinkage being calculated by comparing the measured dimension of an injection moulded box with the nominal mould dimension,.

12. Use of a polymer composition according to any of claims 1 to 9 for the manufacture of polymer articles by injection moulding or compression moulding, thermoforming, blow moulding, film or sheet extrusion, pipe or cable extrusion.

13. The use of claim 12, wherein caps and closures for food, household, hygiene and health-care applications are manufactured.

09/530803

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>BOR 10 PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 98/ 07215</b>	International filing date (day/month/year) <b>09/11/1998</b>	(Earliest) Priority Date (day/month/year) <b>07/11/1997</b>
Applicant <b>BOREALIS A/S et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

---

☐ None of the figures.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 98/07215

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08K5/00 C08L23/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 369 658 A (SUMITOMO) 23 May 1990 see page 2, line 40 - line 45; claims 1-3; examples; table 1 ---	1,4,5
A	EP 0 417 319 A (MITSUBISHI) 20 March 1991 cited in the application see page 2, line 24 - line 35; claims 1,5; examples ---	1,4-7
A	GB 1 104 665 A (ICI LTD.) see page 1, line 19 - line 20 see page 1, line 39 - line 53 see page 1, line 65 - line 70 see page 2, line 24 - line 26 see page 3, line 52 - line 61; claims 1,4,5,11,13,19,34; examples --- -/--	1,4-6,13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance  
"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
"&" document member of the same patent family

Date of the actual completion of the international search

20 April 1999

Date of mailing of the international search report

03/05/1999

Name and mailing address of the ISA  
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Authorized officer

Engel, S

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 98/07215

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 151 883 A (SUMITOMO) 21 August 1985  cited in the application  see page 15, line 23 - page 16, line 2;  claims 1,6-9; examples; table 2  -----</p>	1,4-6

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/07215

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 369658	A	23-05-1990	JP 2135245 A	24-05-1990
			JP 2762492 B	04-06-1998
			CA 2001234 A,C	16-05-1990
			DE 68928768 D	10-09-1998
			DE 68928768 T	14-01-1999
			SG 47424 A	17-04-1998
			US 5032645 A	16-07-1991
			US 5115027 A	19-05-1992
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EP 417319	A	20-03-1991	JP 2793871 B	03-09-1998
			JP 3028246 A	06-02-1991
			JP 3014852 A	23-01-1991
			DE 69028752 D	07-11-1996
			DE 69028752 T	06-03-1997
			US 5286540 A	15-02-1994
			WO 9011328 A	04-10-1991
-----				
GB 1104665	A		BE 679547 A	14-10-1966
			DE 1595842 A	14-05-1970
			FR 1476249 A	21-06-1967
			NL 6605058 A	17-10-1966
-----				
EP 151883	A	21-08-1985	JP 1761591 C	28-05-1993
			JP 3042298 B	26-06-1991
			JP 60139731 A	24-07-1985
			CA 1255048 A	30-05-1989
			CA 1254690 A	23-05-1989
			DE 3471942 A	14-07-1988
			EP 0152701 A	28-08-1985
			SG 96994 G	12-05-1995
			US 4696979 A	29-09-1987
			US 4551501 A	05-11-1985
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The use of vinyl compounds, such as polymers of vinyl cycloalkanes and 3-methyl-1-butene, as nucleating agents in the form of reactor made blends of polypropylene and polymerised vinyl compounds or polypropylene compounds, is suggested in the prior art, cf. EP Patent Specifications Nos. 0 152 701, 0 151 883, 0 368 577 and 0 417 319.

5 However, none of the prior art publications makes any reference to the use of these highly nucleated materials for the production of coloured caps and closures.

According to the present invention it has now surprisingly been found that propylene homo- or copolymers nucleated with a component containing polymerized vinyl compound  
10 units will give excellent dimensional consistency by dominating the pigments' nucleating effect with its strong nucleation. The strongly nucleating effect of the polymeric nucleating agent is apparent from the high crystallisation temperature of the polymer. Thus, the crystallisation temperature of the material is at least 7 °C, preferably 10 °C and in particular over 13 °C higher than the crystallisation temperature of the corresponding non-  
15 nucleated polymer and the material exhibits a fast crystallisation rate. Caps of various colours moulded with a polypropylene nucleated with a polymerised vinyl compound grade to provide a composition according to the present invention will therefore have practically the same dimensions.

20 More specifically, the polymer composition according to the present invention is characterized by what is stated in the characterizing part of claim 1.

The process according to the present invention for preparing coloured polypropylene compositions is characterized by what is stated in the characterizing part of claim 10.  
25

The present compositions can be used in any kind of polymer articles. Particular advantages are obtained by applying the compositions to the manufacture of injection moulded and/or compression moulded products as well as articles produced by thermoforming, blow moulding and film and sheet extrusion.  
30

The invention achieves a number of considerable advantages. In particular it should be pointed out that the strong nucleating effect of a polymeric nucleating agent containing

wherein  $R_1$  and  $R_2$  together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

The following specific examples of vinyl compounds can be mentioned: vinyl  
5 cycloalkanes, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl  
cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene, 3-ethyl-  
1-hexene or mixtures thereof. Vinyl cyclohexane (VCH) is a particularly preferred  
monomer but, for example, 3-methyl-1-butene can be used as a monomer or comonomer to  
adjust the crystallisation temperature.

10 For the purpose of the present invention "nucleated propylene polymer" stands for a  
polymer having an increased and controlled degree of crystallinity preferably amounting to  
over 50 % and preferably having a crystallization temperature of more than 7 °C,  
preferably over 10 °C and in particular over 13 °C of the  $T_{cr}$  of the corresponding non-  
15 nucleated polymer. Using  $MgCl_2$ -supported high-yield Ziegler-Natta catalysts  
crystallization temperatures of more than 120 °C, preferably over 124 °C and in particular  
over 126 °C can be obtained. In compositions containing colouring pigments having a  
nucleating effect, particularly advantageous results are obtained by using polymers having  
a crystallization temperature over 15 °C higher than that of the corresponding non-  
20 nucleated polymer (for a polymer produced with the above-mentioned ZN-catalyst, 128  
°C).

According to a preferred embodiment of the present invention, modification of the catalyst  
by polymerizing a vinyl compound, such as VCH, in the presence thereof is performed in  
25 an inert fluid which does not dissolve the polymer formed (e.g. polyVCH). One  
particularly preferred polymerization medium comprises a viscous substance, in the  
following a "wax", such as an oil or a mixture of an oil with a solid or semi-solid polymer  
(oil-grease). The viscosity of such a viscous substance is usually 1,000 to 15,000 cP (1 - 15  
Ns/m<sup>2</sup>) at room temperature. The advantage of wax prepolymerization is that the catalyst  
30 can be prepolymerized, stored and fed into the process in the same media and catalyst wax  
preparation and prepolymerization is performed in the same process device. Due to the  
fact that no washing, drying, sieving and transferring thus are needed, the catalyst activity

high-yield Ziegler-Natta catalysts, having high stiffness, an increased overall degree of crystallization and a crystallization temperature of the propylene homopolymer fraction of more than 120 °C, preferably over 124 °C and in particular over 126 °C. The degree of crystallization for a propylene homopolymer is generally over 48 %, and often over 50 %.

5

The amount of the nucleating polymeric agent is, in case of propylene polymers or copolymers, about 0.0001 to 1 wt-%, and in case of polypropylene blends about 0.0001 to 0.5 wt-%.

10 This nucleated polypropylene (100 parts by weight) is blended with 0.01 to 5 parts by weight of the coloured pigment of choice. The particle size of the pigment is usually 0.01 to 1000 micrometre and more often 0.1 to 10 micrometre.

15 The colouring agent is usually in the form of a masterbatch comprising also a polymer carrier. The blending with the polypropylene is directly done at the conversion machine (e.g. extruder, injection moulding machine...) by dosing the pigment with a gravimetric side feeder. When the colouring agent is liquid it is dosed with a liquid pump.

20 The present polymers and copolymers of propylene can be blended and optionally compounded with additives and adjuvants conventionally used in the art. Thus, suitable additives include antistatic agents, flame retardants, light and heat stabilizers, reinforcement agents, pigments and carbon black. Fillers such as mica, CaCO<sub>3</sub>, talc and wollastonite can also be used. Further, the polymers and copolymers can be blended with non-nucleated propylene and/or with other polymers, in particular other polyolefins, such as LD-, LLD-, MD- and HD-polyethylenes and polybutylene.

25  
30 Compositions according to the invention containing pigments will exhibit very small variation in shrinkage irrespective of the colouring agent used. As the results indicated below in Table 1 show, the variation in shrinkage in both flow and cross direction is less than 5 % for white, red and blue pigments compared to conventional, non-nucleated polymers having a variation of shrinkage in the range of 10 to 20 %. The fact that the pigments' nucleating effect is clearly dominated by the nucleated polypropylene with its

**IN THE CLAIMS:**

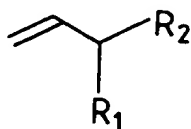
## 1. Coloured polymer composition comprising

- a propylene polymer nucleated with a polymerized vinyl compound and having an at least 7 °C higher crystallization temperature than that of the corresponding non-nucleated polymer, and
- a colour pigment having a concentration of 0.01 to 5 wt-% calculated from the weight of the nucleated propylene polymer.

2. The composition according to claim 1, wherein the colour pigment has a nucleating effect on the propylene polymer.

3. The composition of claim 1 or 2, wherein the shrinkage of the composition, calculated by comparing the measured dimension of an injection moulded box with the nominal mould dimension, varies less than 5 % for different colour pigments.

4. The polymer composition according to claim 1, wherein the propylene polymer contains about 0.0001 to 1 % by weight of units derived from a vinyl compound of the formula



wherein  $R_1$  and  $R_2$  together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

5. The polymer composition according to claim 4, wherein the propylene polymer contains cycloalkane units, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene or 3-ethyl-hexene units or mixtures thereof.

6. The polymer composition according to any of claims 1 to 5, wherein the nucleated

propylene polymer comprises a propylene polymer copolymer polymerized in the presence of a catalyst modified with a polymer containing vinyl compound units.

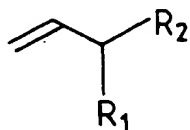
7. The polymer composition according to any of claims 1 to 5, wherein the nucleated propylene polymer comprises a propylene homo- or copolymer blended with a polymer containing polymerised vinyl compound units.

8. The polymer composition according to any of the preceding claims, wherein the pigment is selected from the group of white pigments, yellow/orange pigments, red/violet pigments, blue/green pigments and carbon black.

9. The polymer composition according to claim 8, wherein the pigment is selected from the group of titanium dioxide, isoindolinone, azocondensation, quinacridone, diketo pyrrolo pyrrol, ultramarine blue, Cu Phtalocyanine blue and carbon black.

10. A process for preparing a coloured polymer composition comprising a propylene polymer and a colour pigment, characterized by using a propylene polymer nucleated with a polymerized vinyl compound and having an at least 7 °C higher crystallization temperature than the corresponding non-nucleated polymer, the concentration of the colouring pigment being 0.01 to 5 wt-% calculated from the weight of the nucleated propylene polymer,.

11. The process according to claim 10 wherein 100 parts by weight of a nucleated polypropylene composition containing about 0.0001 to 1 % by weight of units derived from a vinyl compound of the formula



wherein R<sub>1</sub> and R<sub>2</sub> together form a 5 or 6 membered saturated or unsaturated or aromatic

ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms is blended with 0.01 to 5 parts by weight of a colouring pigment selected from the group of white pigments, green pigments, red pigments, blue pigments and carbon black, to provide a coloured polypropylene composition, the shrinkage of which varies less than 5 % for different colour pigments, said shrinkage being calculated by comparing the measured dimension of an injection moulded box with the nominal mould dimension,.

12. Use of a polymer composition according to any of claims 1 to 9 for the manufacture of polymer articles by injection moulding or compression moulding, thermoforming, blow moulding, film or sheet extrusion, pipe or cable extrusion.

13. The use of claim 12, wherein caps and closures for food, household, hygiene and health-care applications are manufactured.

17  
REC'D 10 FEB 2000

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PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BOR 10 PCT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP98/07215	International filing date (day/month/year) 09/11/1998	Priority date (day/month/year) 07/11/1997
International Patent Classification (IPC) or national classification and IPC C08K5/00		
Applicant BOREALIS A/S et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  20/05/1999	Date of completion of this report  08.02.00
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Hein. F  Telephone No. +49 89 2399 2134 

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP98/07215

## I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

### Description, pages:

1,2,4,5,7-12, 14-19 as originally filed

3,6,13 as received on 03/12/1999 with letter of 03/12/1999

### Claims, No.:

1-13 as received on 03/12/1999 with letter of 03/12/1999

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**see separate sheet**

4. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims	1-13
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-13
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-13
	No:	Claims	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP98/07215

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**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**R Item I**

**Basis of the report**

The applicant has not indicated the passage(s) of the application as filed on which the amendments to operative Claims 3 and 11 are based.

These amendments are considered to contravene Art. 34(2)(b) PCT.

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

D1: EP-A-0 152 701 (cited in the application)

D2: EP-A-0 151 883

D3: GB-A-1 104 665

The claimed subject-matter differs from the teaching of D1 - D3 in that the concentration of the colour pigment is defined.

The prior art documents on file are silent on shrinkage problems associated with pigment-containing propylene polymer compositions.

Therefore, the subject-matter of Claims 1-13 is regarded to meet the requirements of Art. 33 (2)-(4) PCT.

**Re Item VIII**

**Certain observations on the international application**

Claims 3 and 11 are unclear since the conditions under which the shrinkage occurs are not defined (Art. 6 PCT).

Reference is made in this respect to the last par. at p. 13, which refers to a variation in shrinkage in both flow and cross direction of less than 5 % for white, red and blue pigments (compared to conventional, non-nucleated polymers).

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ EP

# PCT

## CHAPTER II

### DEMAND

under Article 31 of the Patent Cooperation Treaty:  
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only		
Identification of IPEA		Date of receipt of DEMAND
<b>Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION</b>		Applicant's or agent's file reference BOR 10 PCT
International application No. PCT/EP98/07215	International filing date (day/month/year) (09.11.1998) 9 November 1998	(Earliest) Priority date (day/month/year) (07.11.1997) 7 November 1997
Title of invention Coloured polypropylene compositions		
<b>Box No. II APPLICANT(S)</b>		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)  BOREALIS A/S Lyngby Hovedgade 96 DK-2800 Lyngby Denmark		Telephone No.:
		Facsimile No.:
		Teleprinter No.:
State (that is, country) of nationality: Denmark		State (that is, country) of residence: Denmark
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)  CROZIER, Hérve Ekliveien 37 N-3960 Stathelle Norway		
State (that is, country) of nationality: Norway		State (that is, country) of residence: Norway
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)  FOLLAND, Rick Chemin des Hougardiers 3 Melin B-1370 Jodoigne Belgium		
State (that is, country) of nationality: Belgium		State (that is, country) of residence: Belgium
<input type="checkbox"/> Further applicants are indicated on a continuation sheet.		

**Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE**The following person is ☒ agent ☐ common representativeand ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*LAINE, Seppo; SUNDMAN, Christoffer;  
LIPSANEN, Jari; HOVI, Simo; and  
KNUTH-LEHTOLA, Sisko  
of SEPPO LAINE OY  
Itämerenkatu 3 B, FIN-00180 Helsinki,  
Finland

Telephone No.:

+358-9-68 59 560

Facsimile No.:

+358-9-68 59 56 10

Teleprinter No.:

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.**Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION****Statement concerning amendments:\***

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filedthe description ☐ as originally filed  
☐ as amended under Article 34the claims ☐ as originally filed  
☐ as amended under Article 19 (together with any accompanying statement)  
☐ as amended under Article 34the drawings ☐ as originally filed  
☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

\* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English☒ which is the language in which the international application was filed.☐ which is the language of a translation furnished for the purposes of international search.☐ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.**Box No. V ELECTION OF STATES**The applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes not to elect:

**Box No. VI CHECK LIST**

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- |  |   |        |
|--|---|--------|
| 1. translation of international application                              | : | sheets |
| 2. amendments under Article 34   | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19  | : | sheets |
| 5. letter  | : | sheets |
| 6. other ( <i>specify</i> )  | : | sheets |

For International Preliminary  
Examining Authority use only

received

not received

☐☐☐☐☐☐☐☐☐☐☐☐

The demand is also accompanied by the item(s) marked below:

- |  |   |
|--|---|
| 1. <input checked="" type="checkbox"/> fee calculation sheet                             | 4. <input type="checkbox"/> statement explaining lack of signature                                  |
| 2. <input type="checkbox"/> separate signed power of attorney                            | 5. <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form |
| 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: | 6. <input type="checkbox"/> other ( <i>specify</i> ):   |

**Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

For the Applicants

Seppo Laine Oy

Christoffer Sundman

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

# PCT

## REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum)

BOR 10 PCT

### Box No. I TITLE OF INVENTION

Coloured polypropylene compositions

### Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

BOREALIS A/S  
Lyngby Hovedgade 96  
DK-2800 Lyngby  
Denmark

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State (that is, country) of nationality:  
Denmark

State (that is, country) of residence:  
Denmark

This person is applicant  
for the purposes of:

☐ all designated  
States

☒ all designated States except  
the United States of America

☐ the United States  
of America only

☐ the States indicated in  
the Supplemental Box

### Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

CROZIER, Hérve  
Ekliveien 37  
N-3960 Stathelle  
Norway

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box  
is marked, do not fill in below.)

State (that is, country) of nationality:  
Norway

State (that is, country) of residence:  
Norway

This person is applicant  
for the purposes of:

☐ all designated  
States

☐ all designated States except  
the United States of America

☒ the United States  
of America only

☐ the States indicated in  
the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

### Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf  
of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

LAINE, Seppo; SUNDMAN, Christoffer;  
LIPSANEN, Jari; HOVI, Simo; and  
KNUTH-LEHTOLA, Sisko  
of SEPPO LAINE OY  
Itämerenkatu 3 B, FIN-00180 Helsinki,  
Finland

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Facsimile No.

+358-9-68 59 56 10

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

## Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

FOLLAND, Rick  
Chemin des Hougardiers 3  
Melin  
B-1370 Jodoigne  
Belgium

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
Belgium

State (that is, country) of residence:  
Belgium

This person is applicant  
for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant  
for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant  
for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant  
for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

## Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes: at least one must be marked):

## Regional Patent

- ☒ AP **ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ EA **Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP **European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA **OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

## National Patent (if other kind of protection or treatment desired, specify on dotted line):

- |  |  |
|--|--|
| <input checked="" type="checkbox"/> AL Albania                               | <input checked="" type="checkbox"/> LS Lesotho                                   |
| <input checked="" type="checkbox"/> AM Armenia                               | <input checked="" type="checkbox"/> LT Lithuania                                 |
| <input checked="" type="checkbox"/> AT Austria                               | <input checked="" type="checkbox"/> LU Luxembourg                                |
| <input checked="" type="checkbox"/> AU Australia                             | <input checked="" type="checkbox"/> LV Latvia                                    |
| <input checked="" type="checkbox"/> AZ Azerbaijan                            | <input checked="" type="checkbox"/> MD Republic of Moldova                       |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina                | <input checked="" type="checkbox"/> MG Madagascar                                |
| <input checked="" type="checkbox"/> BB Barbados                              | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BG Bulgaria                              |  |
| <input checked="" type="checkbox"/> BR Brazil                                | <input checked="" type="checkbox"/> MN Mongolia                                  |
| <input checked="" type="checkbox"/> BY Belarus                               | <input checked="" type="checkbox"/> MW Malawi                                    |
| <input checked="" type="checkbox"/> CA Canada                                | <input checked="" type="checkbox"/> MX Mexico                                    |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein  | <input checked="" type="checkbox"/> NO Norway                                    |
| <input checked="" type="checkbox"/> CN China                                 | <input checked="" type="checkbox"/> NZ New Zealand                               |
| <input checked="" type="checkbox"/> CU Cuba                                  | <input checked="" type="checkbox"/> PL Poland                                    |
| <input checked="" type="checkbox"/> CZ Czech Republic                        | <input checked="" type="checkbox"/> PT Portugal                                  |
| <input checked="" type="checkbox"/> DE Germany                               | <input checked="" type="checkbox"/> RO Romania                                   |
| <input checked="" type="checkbox"/> DK Denmark                               | <input checked="" type="checkbox"/> RU Russian Federation                        |
| <input checked="" type="checkbox"/> EE Estonia                               | <input checked="" type="checkbox"/> SD Sudan                                     |
| <input checked="" type="checkbox"/> ES Spain                                 | <input checked="" type="checkbox"/> SE Sweden                                    |
| <input checked="" type="checkbox"/> FI Finland                               | <input checked="" type="checkbox"/> SG Singapore                                 |
| <input checked="" type="checkbox"/> GB United Kingdom                        | <input checked="" type="checkbox"/> SI Slovenia                                  |
| <input checked="" type="checkbox"/> GE Georgia                               | <input checked="" type="checkbox"/> SK Slovakia                                  |
| <input checked="" type="checkbox"/> GH Ghana                                 | <input checked="" type="checkbox"/> SL Sierra Leone                              |
| <input checked="" type="checkbox"/> GM Gambia                                | <input checked="" type="checkbox"/> TJ Tajikistan                                |
| <input type="checkbox"/> GW Guinea-Bissau                                    | <input checked="" type="checkbox"/> TM Turkmenistan                              |
| <input checked="" type="checkbox"/> HR Croatia                               | <input checked="" type="checkbox"/> TR Turkey                                    |
| <input checked="" type="checkbox"/> HU Hungary                               | <input checked="" type="checkbox"/> TT Trinidad and Tobago                       |
| <input checked="" type="checkbox"/> ID Indonesia                             | <input checked="" type="checkbox"/> UA Ukraine                                   |
| <input checked="" type="checkbox"/> IL Israel                                | <input checked="" type="checkbox"/> UG Uganda                                    |
| <input checked="" type="checkbox"/> IS Iceland                               | <input checked="" type="checkbox"/> US United States of America                  |
| <input checked="" type="checkbox"/> JP Japan                                 |  |
| <input checked="" type="checkbox"/> KE Kenya                                 | <input checked="" type="checkbox"/> UZ Uzbekistan                                |
| <input checked="" type="checkbox"/> KG Kyrgyzstan                            | <input checked="" type="checkbox"/> VN Viet Nam                                  |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> YU Yugoslavia                                |
|  | <input checked="" type="checkbox"/> ZW Zimbabwe                                  |
| <input checked="" type="checkbox"/> KR Republic of Korea                     |  |
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<b>(21) International Application Number:</b> PCT/EP98/07215 <b>(22) International Filing Date:</b> 9 November 1998 (09.11.98) <b>(30) Priority Data:</b> 974177 7 November 1997 (07.11.97) FI <b>(71) Applicant (for all designated States except US):</b> BOREALIS A/S [DK/DK]; Lyngby Hovedgade 96, DK-2800 Lyngby (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CROZIER, Hérve [NO/NO]; Ekliveien 37, N-3960 Stathelle (NO). FOLLAND, Rick [BE/BE]; Chemins des Hougardiers 3, Melin, B-1370 Jodoigne (BE). <b>(74) Agents:</b> LAINE, Seppo et al.; Seppo Laine Oy, Itämerenkatu 3 B, FIN-00180 Helsinki (FI).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW; ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> COLOURED POLYPROPYLENE COMPOSITIONS  <b>(57) Abstract</b>  The present invention concerns coloured polymer compositions and a process for the preparation thereof. The present composition comprises a propylene polymer nucleated with a polymeric nucleating agent containing vinyl compound units and having an at least 7 °C higher crystallization temperature than that of the corresponding non-nucleated polymer, and a colour pigment having a nucleating effect on the propylene polymer. The shrinkage of the composition varies less than 5 % for different colour pigments.		

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**COLOURED POLYPROPYLENE COMPOSITIONS****Background of the Invention****Field of the Invention**

The present invention relates to coloured polymer compositions. In particular, the present invention concerns compositions of propylene homo- and copolymers suitable for caps and closures and similar polymer articles. The invention also concerns a process for preparing such compositions. Finally, the present invention relates to the use of the new propylene polymers or copolymers for the manufacture of products by melt stage processing, e.g., by blow moulding, thermoforming, injection moulding and sheet or film extrusion.

**Description of Related Art**

To an increasing extent, caps and closures of various design for drinks, food, household, hygiene, health-care, oils and chemicals and other applications are nowadays manufactured from polymeric materials. This is partly due to the requirement for high productivity, i.e. short processing cycle, which becomes crucial for the mass production of carbonated soft drinks caps that are usually obtained by either injection moulding or compression moulding techniques.

Propylene homo- and copolymers having excellent resistance to heat and chemicals as well as attractive mechanical properties, such as stiffness and impact resistance, are becoming a particularly interesting materials for these applications.

There are, however, some problems related to the prior art. Thus, nearly all caps and closures manufactured from polymeric materials are coloured. It has been experienced that pigments may have a nucleating effect on polypropylene and variation in intensity of this effect from one colour to another will result in dimensional variations because of differences in the shrinkage associated with the nucleation.

### Summary of the Invention

It is an object of the present invention to eliminate the problems related to the prior art and to provide novel coloured polypropylene compositions having consistent shrinkage and improved mechanical properties highly suited to the manufacture of injection moulded or compression moulded products which can be used as caps and closures.

A second object of the invention is to provide a process for preparing novel polypropylene compositions of the above kind.

It is still a further object of the present invention to provide products of polypropylene compositions by injection moulding or compression moulding techniques.

These and other objects, together with the advantages thereof over known processes and products, which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

The invention is based on blending colouring pigments with propylene homo- or copolymers nucleated for high crystallinity. In connection with the present invention it has been found that nucleating the PP resin may reduce the differences between the various degrees of shrinkage of polymer compositions coloured with different pigments. However, conventional inorganic or organic nucleating agents, e.g. talc, are either too weak to have a dominating effect or they can give rise to undesired reactions with the pigments. The conventional agents can also be difficult to disperse and there can be restrictions on food contact approvals (e.g. NaBz). Some are non-economical (e.g. sorbitol derivatives) for use for PP for caps and closures.

According to the present invention, the pigments are therefore blended with propylene polymers or copolymers nucleated with polymeric vinyl compounds to provide coloured polypropylene compositions having a consistent shrinkage during melt processing irrespective of the colouring pigment used.

The use of vinyl compounds, such as polymers of vinyl cycloalkanes and 3-methyl-1-butene, as nucleating agents in the form of reactor made blends of polypropylene and polymerised vinyl compounds or polypropylene compounds, is suggested in the prior art. cf. EP Patent Specifications Nos. 0 152 701, 0 151 883, 0 368 577 and 0 417 319.

5 However, none of the prior art publications makes any reference to the use of these highly nucleated materials for the production of coloured caps and closures.

According to the present invention it has now surprisingly been found that propylene homo- or copolymers nucleated with a component containing polymerized vinyl compound  
10 units will give excellent dimensional consistency by dominating the pigments' nucleating effect with its strong nucleation. The strongly nucleating effect of the polymeric nucleating agent is apparent from the high crystallisation temperature of the polymer. Thus, the crystallisation temperature of the material is at least 7 °C, preferably 10 °C and in particular over 13 °C higher than the crystallisation temperature of the corresponding non-  
15 nucleated polymer and the material exhibits a fast crystallisation rate. Caps of various colours moulded with a polypropylene nucleated with a polymerised vinyl compound grade to provide a composition according to the present invention will therefore have practically the same dimensions.

20 More specifically, the polymer composition according to the present invention is characterized by what is stated in the characterizing part of claim 1.

The process according to the present invention for preparing coloured polypropylene compositions is characterized by what is stated in the characterizing part of claim 9.  
25

The present compositions can be used in any kind of polymer articles. Particular advantages are obtained by applying the compositions to the manufacture of injection moulded and/or compression moulded products as well as articles produced by thermoforming, blow moulding and film and sheet extrusion.  
30

The invention achieves a number of considerable advantages. In particular it should be pointed out that the strong nucleating effect of a polymeric nucleating agent containing

polymerized vinyl compound units will give potential for cycle time reduction because solidification in the mould will happen earlier and faster compared to any other PP grade nucleated with conventional nucleating agents. There are also other benefits of the present invention compared to the use of additive nucleating agents that are of particular interest for the manufacture of caps and closures: the invention will provide for a reduction of the number and amount of additives. The polymeric nucleating agents are inert towards other additives/pigments, they give no taste and odour, no migration / plate out, excellent dispersion of the nucleating effect and more consistent nucleation. These positive effects are accompanied with clearly smaller amounts of the polymeric nucleating agents compared to additive nucleation.

The characteristics of the polymer compositions can easily be tailored in respect to MFR, type of polymer (homopolymer, copolymer, impact modified ...) as well as in respect to physical properties.

Next, the invention will be more closely examined with the aid of the following detailed description.

### **Detailed Description of the Invention**

The compositions of the present invention include a polymeric component comprising a propylene polymer nucleated with polymerized vinyl compounds together with at least one colouring agent. The compositions can contain other components known in the art, such as adjuvants, additives and fillers.

The colouring agent used in the present invention can be any colouring pigment, organic or inorganic, having a nucleating effect of various strength on propylene homo- or copolymers. By dominating the nucleating effect, if any, of the pigment, the nucleated propylene homo- or copolymer will provide a controlled and predictable shrinkage irrespective of the pigment.

Examples of colouring pigments are white pigments, such as titanium dioxide,

yellow/orange pigments such as isoindolinone or azocondensation, red/violet such as quinacridone or diketo pyrrolo pyrol, blue/green pigments such as ultramarine blue or Cu Phtalocyanine blue, and black pigments such as carbon black. The amount of pigments is usually 0.01 to 5 % by weight of the polypropylene component.

5

For the purpose of the present invention, the terms "colouring agent" and "colouring pigment" are interchangeably used for designating any material used to give the final product a desired colour which is different from the one it would have without the use of that specific material.

10

The main component of the present compositions is the nucleated propylene polymer which contains a polymerized vinyl compound in an amount of 0.0001 to 1 %, in particular about 5 to 1000 ppm, by weight of the composition. By this nucleation it is possible to attain a polypropylene having a high degree of crystallinity, a high crystallization temperature, small crystal size and a great crystallization rate. These kinds of compositions can be used for the preparation of moulded products. They exhibit improved optical and physical properties.

15

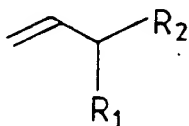
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The nucleation of the propylene polymers can be carried out by modifying the polymerization catalyst with vinyl compounds and using the modified catalyst for polymerization of propylene optionally in the presence of comonomers to provide a propylene homopolymer or copolymer containing about 0.0001 to 1 % (calculated from the weight of the composition) polymerized vinyl compounds. Another approach for nucleating propylene polymers comprises blending polypropylene with polymers containing vinyl compound units.

25

For the purpose of the present invention "vinyl compounds" are compounds having the formula I

30





wherein  $R_1$  and  $R_2$  together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

The following specific examples of vinyl compounds can be mentioned: vinyl cycloalkanes, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene, 3-ethyl-1-hexene or mixtures thereof. Vinyl cyclohexane (VCH) is a particularly preferred monomer but, for example, 3-methyl-1-butene can be used as a monomer or comonomer to adjust the crystallisation temperature.

For the purpose of the present invention "nucleated propylene polymer" stands for a polymer having an increased and controlled degree of crystallinity preferably amounting to over 50 % and preferably having a crystallization temperature of more than 7 °C, preferably over 10 °C and in particular over 13 °C of the  $T_{cr}$  of the corresponding non-nucleated polymer. Using  $MgCl_2$ -supported high-yield Ziegler-Natta catalysts crystallization temperatures of more than 120 °C, preferably over 124 °C and in particular over 126 °C can be obtained. In compositions containing colouring pigments having a nucleating effect, particularly advantageous results are obtained by using polymers having a crystallization temperature over 15 °C higher than that of the corresponding non-nucleated polymer (for a polymer produced with the above-mentioned ZN-catalyst, 128 °C).

According to a preferred embodiment of the present invention, modification of the catalyst by polymerizing a vinyl compound, such as VCH, in the presence thereof is performed in an inert fluid which does not dissolve the polymer formed (e.g. polyVCH). One particularly preferred polymerization medium comprises a viscous substance, in the following a "wax", such as an oil or a mixture of an oil with a solid or semi-solid polymer (oil-grease). The viscosity of such a viscous substance is usually 1,000 to 15,000 cP at room temperature. The advantage of wax prepolymerization is that the catalyst can be prepolymerized, stored and fed into the process in the same media and catalyst wax preparation and prepolymerization is performed in the same process device. Due to the fact that no washing, drying, sieving and transferring thus are needed, the catalyst activity

is maintained (cf. Finnish Patent No. 95387). The present process is inexpensive because high catalyst concentrations and high PP production capacities can be used. Also the amount of waste is diminished because the medium used during polymerization of the vinyl compound does not have to be removed.

5

According to another preferred embodiment, the method for improving the crystallinity and transparency of polypropylene by blending a crystalline polypropylene with a vinyl cycloalkane polymer is carried out by melt-kneading the crystalline polypropylene with the crystal nucleating agent, compounding the crystal nucleating agent or reactor made blend of the crystal nucleating agent and PP with the crystalline polypropylene and melt kneading the mixture during film formation, and compounding the master batch of the crystal nucleating agent with the crystalline polypropylene.

10

15

The vinyl compound units of the blending and compounding process can be derived from any of the units identified in the above formula I in connection with the first embodiment of the invention.

20

As catalyst any stereospecific catalyst for propylene polymerization can be used, which is capable of catalyzing polymerization and copolymerization of propylene and comonomers at a pressure of 10 to 100 bar, in particular 25 to 80 bar, and at a temperature of 40 to 110 °C, in particular 60 to 110 °C. Ziegler-Natta as well as metallocene catalysts can be used.

25

Generally, the Ziegler-Natta catalyst used in the present invention comprises a catalyst component, a cocatalyst component, an external donor, the catalyst component of the catalyst system primarily containing magnesium, titanium, halogen and an internal donor.

Examples of suitable catalyst systems are described in, for example, Finnish Patents Nos. 86866, 96615 and 88047 and 88048.

30

One particularly preferable catalyst, which can be used in the present invention, is disclosed in FI Patent No. 88047. Another preferred catalyst is disclosed in Finnish Patent Application No. 963707.

A catalyst system useful in the present process can be prepared by reacting a magnesium halide compound with titanium tetrachloride and an internal donor. The magnesium halide compound is, for example, selected from the group of magnesium chloride, a complex of magnesium chloride with a lower alkanol and other derivatives of magnesium chloride.

5  $\text{MgCl}_2$  can be used as such or it can be combined with silica, e.g. by absorbing the silica with a solution or slurry containing  $\text{MgCl}_2$ . The lower alkanol used can be preferably methanol or ethanol, particularly ethanol.

10 The titanium compound used in the preparation of the procatalyst is preferably an organic or inorganic titanium compound, having an oxidation state of titanium of 3 or 4. Also other transition metal compounds, such as vanadium, zirconium, chromium, molybdenum and tungsten compounds can be mixed with the titanium compound. The titanium compound usually is halide or oxyhalide, an organic metal halide, or a purely metal organic compound, in which only organic ligands have been attached to the transition metal.

15 Particularly preferable are the titanium halides, especially  $\text{TiCl}_4$ . Preferably the titaniation is carried out in two or three steps.

20 The Ziegler-Natta catalyst used can also be an heterogeneous unsupported  $\text{TiCl}_3$  based catalyst. This kind of catalysts are typically solid  $\text{TiCl}_3$  in a delta crystalline form which are activated with aluminium-chloride-alkyls, such as diethylaluminiumchloride. The solid  $\text{TiCl}_3$  catalyst are typically prepared by reduction of  $\text{TiCl}_4$  with aluminium-alkyls and/or aluminium-chloride-alkyls, possibly combined with heat treatment to maximise the desired delta crystalline form of  $\text{TiCl}_3$ . The performance, especially stereospecificity, of these catalyst can be improved by using Lewis-bases (electron donors), such as esters, ethers or

25 amines.

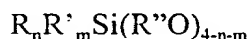
The activity and stereospecificity of these heterogeneous unsupported  $\text{TiCl}_3$  based catalysts are typically so low that propylene polymers or copolymers prepared require purification from catalyst residues and removal of some atactic non-crystalline polymer.

30 The alkoxy group of the phthalic acid ester used comprises at least five carbon atoms, preferably at least 8 carbon atoms. Thus, as the ester can be used for example propylhexyl

phthalate, dioctyl phthalate, dinonyl phthalate, diisodecyl phthalate, di-undecyl phthalate, ditridecyl phthalate or ditetradecyl phthalate.

The partial or complete transesterification of the phthalatic acid ester can be carried out e.g. by selecting a phthalic acid ester - a lower alcohol pair, which spontaneously or with the aid of a catalyst, which does not damage the procatalyst composition, transesterifies the catalyst at an elevated temperatures. It is preferable to carry out the transesterification at a temperature, which lies in the range of 110 to 150 °C, preferably 120 to 140 °C.

The catalyst prepared by the method above is used together with an organometallic cocatalyst and with an external donor. Generally, the external donor has the formula IV



wherein

R and R' can be the same or different and they stand for a linear, branched or cyclic aliphatic, or aromatic group;

R'' is methyl or ethyl;

n is an integer 0 to 3;

m is an integer 0 to 3; and

n+m is 1 to 3.

The aliphatic groups in the meanings of R and R' can be saturated or unsaturated. Linear C<sub>1</sub> to C<sub>12</sub> hydrocarbons include methyl, ethyl, propyl, butyl, octyl and decanyl. As examples of suitable saturated branched C<sub>1-8</sub> alkyl groups, the following can be mentioned: isopropyl, isobutyl, isopentyl, tert-butyl, tert-amyl and neopentyl. Cyclic aliphatic groups containing 4 to 8 carbon atoms comprise, e.g., cyclopentyl, cyclohexyl, methyl cyclopentyl and cycloheptyl.

A group of interesting donors is formed by strongly co-ordinating donors which form relatively strong complexes with catalyst surface, mainly with MgCl<sub>2</sub> surface in the presence of aluminium alkyl and TiCl<sub>4</sub>. The donor components are characterised by a

strong complexation affinity towards catalyst surface and a sterically large and protective hydrocarbon (R'). Such external donors can be selected from the group consisting of dicyclopentyl dimethoxysilane, diisopropyl dimethoxysilane, di-isobutyl dimethoxysilane, and di-t-butyl dimethoxysilane.

5

An organoaluminum compound is used as a cocatalyst. The organoaluminium compound is preferably selected from the group consisting of trialkylaluminium, dialkyl aluminium chloride and alkyl aluminium sesquichloride.

10

The metallocene catalyst comprises a metallocene/activator reaction product impregnated in a porous support at maximum internal pore volume. The catalyst complex comprises a ligand which is typically bridged, and a transition metal of group IVA...VIA, typically a metal halide, and aluminium alkyl. The ligands can belong to group of heterocyclic substituted or unsubstituted compounds, e.g. indocenes, naftenes, or any other bulky compound which can control the stereoselectivity of the catalyst especially when ligands are bridged together with silane or other chemical bond. The activator is selected from a group in which are derivatives of water and aluminium alkyls e.g. trimethyl aluminium, triethyl aluminium, and tri t-butyl aluminium, or another compound capable of activating the complex. The metallocene/activator reaction product, a solvent capable of dissolving it, and a porous support are brought into mutual contact, the solvent is removed and the porous support is impregnated with the metallocene/activator reaction product, the maximum amount of which corresponds to the pore volume support, cf. International PCT Application No. PCT/FI94/00499.

20

25

One typical structure of metallocene compound is bridged bis(2-R-4-R'-indenyl) M Cl<sub>2</sub>, wherein both R and R' are aliphatic, cycloaliphatic or aromatic hydrocarbons having 1 to 18 C atoms. R' is typically phenyl or naphthyl, and R is typically methyl or ethyl. M is a transition metal, typically titanium, zirconium or hafnium. R and R' may contain heteroatoms, such as silicon, nitrogen, phosphorous or germanium. The bridge between the indenyls is made from 1 to 3 atoms, such as carbon, silicon, nitrogen, phosphorous or germanium. A typical bridge is dimethylsilyl or ethyl. An example of such a metallocene compound is dimethylsilyl-bis(2-methyl-4-phenyl-indenyl)zirconium dichloride.

30

Following the modification of the catalyst with the vinyl compound of the first preferred embodiment of the invention, the catalyst is optionally prepolymerized with propylene and/or another 1-olefin to provide a prepolymerized catalyst composition which is used for polymerization of propylene optionally together with comonomers.

5

The propylene homo- or copolymer can have a unimodal or bimodal molar mass distribution. Thus, the equipment of the polymerization process can comprise any polymerization reactors of conventional design for producing propylene homo- or copolymers. For the purpose of the present invention, "slurry reactor" designates any reactor, such as a continuous or simple batch stirred tank reactor or loop reactor, operating in bulk or slurry and in which the polymer forms in particulate form. "Bulk" means a polymerization in reaction medium that comprises at least 60 wt-% monomer. According to a preferred embodiment the slurry reactor comprises a bulk loop reactor. By "gas phase reactor" is meant any mechanically mixed or fluid bed reactor. Preferably the gas phase reactor comprises a mechanically agitated fluid bed reactor with gas velocities of at least 0.2 m/sec.

Thus, the polymerization reactor system can comprise one or more conventional stirred-tank slurry reactors, as described in WO 94/26794, or one or more gas phase reactors. Preferably the reactors used are selected from the group of loop and gas phase reactors and, in particular, the process employs at least one loop reactor and at least one gas phase reactor. This alternative is particularly suitable for producing bimodal poly-propylene. By carrying out the polymerization in the different polymerization reactors in the presence of different amounts of hydrogen, the MWD (molecular mass distribution) of the product can be broadened and its mechanical properties improved. It is also possible to use several reactors of each type, e.g. one loop reactor and two or three gas phase reactors or two loop reactors and one gas phase reactor, in series.

In every polymerization step it is possible to use also comonomers selected from the group of ethylene, propylene, butene, pentene, hexene and alike as well as their mixtures.

30

In addition to the actual polymerization reactors used for producing the propylene homo-

or copolymer, the polymerization reaction system can also include a number of additional reactors, such as pre- and/or postreactors. The prereactors include any reactor for prepolymerizing the catalyst with propylene and/or other 1-olefins. The postreactors include reactors used for modifying and improving the properties of the polymer product.

5 All reactors of the reactor system are preferably arranged in series.

The gas phase reactor can be an ordinary fluidized bed reactor, although other types of gas phase reactors can be used. In a fluidized bed reactor, the bed consists of the formed and growing polymer particles as well as still active catalyst come along with the polymer

10 fraction. The bed is kept in a fluidized state by introducing gaseous components, for instance monomer on such flowing rate which will make the particles act as a fluid. The fluidizing gas can contain also inert carrier gases, like nitrogen and also hydrogen as a modifier. The fluidized gas phase reactor can be equipped with a mechanical mixer.

15 The gas phase reactor used can be operated in the temperature range of 50 to 115 °C, preferably between 60 and 110°C and the reaction pressure between 5 and 50 bar and the partial pressure of monomer between 2 and 45 bar.

The pressure of the effluent, i.e. the polymerization product including the gaseous reaction

20 medium, can be released after the gas phase reactor in order optionally to separate part of the gaseous and possible volatile components of the product, e.g. in a flash tank. The overhead stream or part of it is recirculated to the reactor.

The propylene homo- or copolymer produced preferably has a MWD of 2 - 10 and a MFR<sub>2</sub> in the range of 0.01 - 1500 g/10 min., in particular 0.05 - 500 g/10 min. MFR<sub>2</sub> values

25 disclosed herein are measured according to ISO 1133, 230 °C, using 2.16 kg load.

In the second embodiment of the invention, wherein a uni- or bimodal propylene homo- or copolymer is blended and compounded with a polymer comprising vinyl compound units,

30 the blending is carried out as known in the art using said nucleating polymeric agent.

By means of both embodiments, a propylene homopolymer or copolymer is produced with

high-yield Ziegler-Natta catalysts, having high stiffness, an increased overall degree of crystallization and a crystallization temperature of the propylene homopolymer fraction of more than 120 °C, preferably over 124 °C and in particular over 126 °C. The degree of crystallization for a propylene homopolymer is generally over 48 %, and often over 50 %.

5

The amount of the nucleating polymeric agent is, in case of propylene polymers or copolymers, about 0.0001 to 1 wt-%, and in case of polypropylene blends about 0.0001 to 0.5 wt-%.

10

This nucleated polypropylene (100 parts by weight) is blended with 0.01 to 5 parts by weight of the coloured pigment of choice. The particle size of the pigment is usually 0.01 to 1000 micrometre and more often 0.1 to 10 micrometre.

15

The colouring agent is usually in the form of a masterbatch comprising also a polymer carrier. The blending with the polypropylene is directly done at the conversion machine (e.g. extruder, injection moulding machine...) by dosing the pigment with a gravimetric side feeder. When the colouring agent is liquid it is dosed with a liquid pump.

20

The present polymers and copolymers of propylene can be blended and optionally compounded with additives and adjuvants conventionally used in the art. Thus, suitable additives include antistatic agents, flame retardants, light and heat stabilizers, reinforcement agents, pigments and carbon black. Fillers such as mica, CaCO<sub>3</sub>, talc and wollastonite can also be used. Further, the polymers and copolymers can be blended with non-nucleated propylene and/or with other polymers, in particular other polyolefins, such as LD-, LLD-, MD- and HD-polyethylenes and polybutylene.

25

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Compositions according to the invention containing pigments will exhibit very small variation in shrinkage irrespective of the colouring agent used. As the results indicated below in Example 1 show, the variation in shrinkage in both flow and cross direction is less than 5 % for white, red and blue pigments compared to conventional, non-nucleated polymers having a variation of shrinkage in the range of 10 to 20 %. The fact that the pigments' nucleating effect is clearly dominated by the nucleated polypropylene with its



strong nucleation is apparent from the results showing that the shrinkage is practically constant irrespective of whether or not the compositions contain any colouring pigment at all. This feature is rather surprising in particular when comparing the shrinkage of the present compositions to conventional talc-nucleated homopolymer compositions which have the same variation as non-nucleated polymer compositions (or even greater) in transversal direction to the flow.

The homopolymer or copolymer composition thus obtained can be used for the manufacture of moulded articles. in particular articles processed by blow moulding, injection moulding, compression moulding, thermoforming and sheet or film extrusion, pipe and cable extrusion.

Particularly useful products include caps and closures for various food, in particular carbonated soft drinks, household, hygiene, health-care and other applications. Further interesting products and articles include bottles, containers and pails.

### **Examples**

The following non-limiting examples illustrate the invention.

#### **Example 1**

Catalyst modification with polymerisation of vinyl cycloalkane:

A high yield  $\text{MgCl}_2$  supported  $\text{TiCl}_4$  Ziegler-Natta catalyst prepared according to Finnish patent FI 88047 was dispersed into a mixture of oil and crease (Shell Ondina Oil N 68 and Fuchs Vaseline Grease SW in 3.2:1 Oil/grease volume ratio). The titanium content of the catalyst was 2.5 wt-%. and the concentration of the catalyst in oil-grease mixture was 176 g cat/dm<sup>3</sup>. Triethylaluminium (TEAL) was added to the catalyst dispersion in a TEAL to titanium mole ratio of 1.5. After that vinylcyclohexane (VCH) was added to the reaction mixture. and the VCH to catalyst weight ratio was 1:1. The reaction mixture was mixed in a temperature of 55 °C until the concentration of unreacted VCH in the reaction mixture

was 350 ppm by weight.

### Example 2

#### Polymerisation of propylene

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The modified catalyst in the oil grease mixture (catalyst mud) obtained from example 1, TEAL, dicyclopentylmethoxysilane and propylene were continuously fed to a process consisting of a prepolymerisation reactor and a loop reactor.

10

Before mixing, the TEAL and dicyclopentylmethoxysilane in a 10.7 w/w ratio was contacted with the catalyst mud. After that the mixture was transferred with propylene, containing the desired amount of hydrogen as molecular weight regulating agent, to a continuous, stirred prepolymerisation reactor. After the prepolymerisation, the reaction mixture together with additional propylene and hydrogen was fed to a continuous loop reactor operating at 68 °C. The obtained PP homo-polymer-propylene slurry containing the catalyst was continuously recovered from the loop reactor to a flashing unit where the liquid propylene was vaporised and the remaining solid polymer particles were continuously recovered from the flashing unit. After purging the unreacted monomers, the required stabilisers and other additives were added and the polymer powder was pelletised with an extruder.

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The final polymer had an MFR<sub>2</sub> of 25 g/10 min, and insolubles in boiling n-heptane 96.0 wt-%.

25

### Example 3

#### Dimensional consistency

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The PP homopolymer described in previous examples and a commercial non nucleated PP homopolymer (MFR 12) and a commercial talc-nucleated PP homopolymer (MFR35) were moulded by injection moulding (machine: Netstal 300 tons, N1570/300MPS) in the form of a box bac characterised by:

- thickness: 1.8 mm

- length: 370 mm
- width: 185 mm
- height: 95 mm
- injection: cold runner
- 5 • max flow length: 300 mm

4 preparations for each of the 3 polypropylenes were moulded:

1. natural
2. 100 parts by weight + 2 parts by weight of white masterbatch (titanium dioxide based  
10 white pigment)
3. 100 parts by weight + 2 parts by weight of red masterbatch (quinacridone based red  
pigment)
4. 100 parts by weight + 2 parts by weight of dark blue masterbatch (Cu Phtalocyanine  
blue based blue pigment)

15 The preparations were blended batch-wise in a bag to prepare roughly 5 kg for each.

Typical moulding conditions were:

- Injection speed: 100 mm/sec
- Holding pressure: 300 bar
- 20 • holding pressure time: 12 sec
- cooling time: 15 sec
- cycle time: 35 sec

25 Dimension of the boxes were measured with an optical device between lines of grid both in  
flow and in transverse direction.

Shrinkage, reported in Table 1, is calculated by comparing the dimension measured to the  
nominal mould dimension. The cross direction has proved to be determinant in  
characterising the shrinkage behaviour of a PP material.

**Table 1. Shrinkage (%) measured on injection moulded boxes of constant weight**

	Grade	Colour	Shrinkage (%)	
			Flow direction	Cross direction
5	Homopolymer of Example 2	Natural	1.68	1.90
		White	1.68	1.95
		Red	1.70	1.93
		Blue	1.70	1.90
		Delta Max	0.02	0.05
10	Non-nucleated PP homopolymer	Natural	1.71	1.58
		White	1.63	1.64
		Red	1.71	1.74
		Blue	1.79	1.96
		Delta Max	0.16	0.38
15	Talc-nucleated PP homopolymer	Natural	1.59	1.54
		White	1.62	1.55
		Red	1.63	1.71
		Blue	1.63	1.96
		Delta Max	0.04	0.41

The non-nucleated PP homopolymer shrank to different extent with different colours. That also attested the different nucleating effect of the different pigments which were also confirmed by measuring crystallisation temperatures of the coloured boxes which were 115.8 °C, 115.7 °C, 119.5 °C and 129.3 °C for the natural, white, red, and blue respectively. Crystallisation temperature was measured by differential scanning calorimetry by weighting 3 mg sample placed in a furnace heated at 10 °C/min from room temperature to 220 °C and then cooled at 10 °C/min to room temperature to get the crystallisation exothermic peak from which the maximum gives the crystallisation temperature.

The talc-nucleated PP homopolymer behaved similarly to the non-nucleated PP homopolymer in the ESNs that shrinkage also varied a lot depending on the colour.

The PP homopolymer (related to the present invention) exhibited practically the same shrinkage, hence the same box dimension. for all the preparations.

#### Example 4

##### 5 Cycle time

The three PP homopolymer samples mentioned in Example 3 were injection moulded in the form of caps on a Netstal 120 tons, HP 1200/445. The mould was a 3 plate mould with 4 cavities, and unscrewing of the cap's threads. The caps were oval, with inner threads,  
10 with a hinged flip top. Dimension were: length 50 mm, height 30 mm, width 38 mm, wall thickness 1.2 mm.

Table 2 indicates the moulding parameters.

15 **Table 2. Moulding parameters**

		PP homopolymer of Example 2	non-nucleated PP homopolymer	talc-nucleated PP homopolymer
MFR	g/10 min	25	12	35
injection speed	mm/ min	50	50	50
holding pressure	bar	300	500	300
holding pressure time	sec	3	3	3
cooling time	sec	9	11.5	10.5
CYCLE TIME	SEC	18.5	21	20

25

The polypropylene nucleated with a polymerised vinyl compound could be moulded with faster cycle because it started to freeze (crystallise) in the mould earlier and faster than the  
30 non-nucleated and talc-nucleated PP homopolymers. Shortest cycle time was determined by decreasing cooling time until the caps deformed at ejection because they were not solidified enough.

Example 5

## Dimensional consistency

The three PP homopolymer samples of Example 3 were also injection moulded according to Example 4. The conditions were identical except for the cooling time which was 11.5 seconds for all them, for the natural but also with red and blue coloured specimens prepared as described in Example 3.

Shrinkage was measured with the height of the caps, compared to the nominal dimension.

**Table 3. Shrinkage in %**

	Natural	Red	Blue
PP homopolymer of Example 2	1.80	1.80	1.80
non-nucleated PP homopolymer	1.25	1.41	1.71
talc-nucleated PP homopolymer	1.35	1.41	1.71

As observed in Example 3, the polypropylene nucleated with a polymerised vinyl compound is superior to the non-nucleated and the talc-nucleated PP homopolymers in the sense that shrinkage, hence dimension, was equal for natural, red and blue caps. On the other hand, variation was observed in dimension for the non-nucleated and talc-nucleated natural, red, and blue caps.

## IN THE CLAIMS:

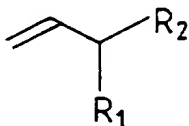
1. Coloured polymer composition comprising

- a propylene polymer nucleated with a polymeric nucleating agent containing vinyl compound units and having an at least 7 °C higher crystallization temperature than that of the corresponding non-nucleated polymer, and
- a colour pigment.

2. The composition according to claim 1, wherein the colour pigment has a nucleating effect on the propylene polymer.

3. The composition of claim 1 or 2, wherein the shrinkage of the composition varies less than 5 % for different colour pigments.

4. The polymer composition according to claim 1, wherein the propylene polymer contains about 0.0001 to 1 % by weight of units derived from a vinyl compound of the formula



wherein R<sub>1</sub> and R<sub>2</sub> together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms.

5. The polymer composition according to claim 4, wherein the propylene polymer contains cycloalkane units, in particular vinyl cyclohexane, vinyl cyclopentane, vinyl-2-methyl cyclohexane and vinyl norbornane, 3-methyl-1-butene, styrene, p-methyl-styrene or 3-ethyl-hexene units or mixtures thereof.

6. The polymer composition according to any of claims 1 to 5, wherein the nucleated propylene polymer comprises a propylene polymer copolymer polymerized in the presence of a catalyst modified with a polymer containing vinyl compound units.

7. The polymer composition according to any of claims 1 to 5, wherein the nucleated propylene polymer comprises a propylene homo- or copolymer blended with a polymer containing polymerised vinyl compound units.

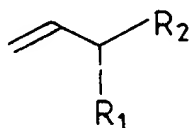
8. The polymer composition according to any of the preceding claims, wherein the pigment is selected from the group of white pigments, yellow/orange pigments, red/violet pigments, blue/green pigments and carbon black.

9. The polymer composition according to claim 8, wherein the pigment is selected from the group of titanium dioxide, isoindolinone, azocondensation, quinacridone, diketo pyrrolo pyrrol, ultramarine blue, Cu Phtalocyanine blue and carbon black.

10. The polymer composition according to any of the preceding claims, wherein the concentration of the colouring pigment is 0.01 to 5 wt-% calculated from the weight of the polypropylene component.

11. A process for preparing a coloured polymer composition comprising a propylene polymer and a colour pigment, characterized by using a propylene polymer nucleated with a polymeric nucleating agent containing vinyl compound units and having an at least 7 °C higher crystallization temperature than the corresponding non-nucleated polymer.

12. The process according to claim 11 wherein 100 parts by weight of a nucleated polypropylene composition containing about 0.0001 to 1 % by weight of units derived from a vinyl compound of the formula



wherein  $\text{R}_1$  and  $\text{R}_2$  together form a 5 or 6 membered saturated or unsaturated or aromatic ring or they stand independently for a lower alkyl comprising 1 to 4 carbon atoms is blended with 0.01 to 5 parts by weight of a colouring pigment selected from the group of white pigments, green pigments, red pigments, blue pigments and carbon black, to provide



a coloured polypropylene composition, the shrinkage of which varies less than 5 % for different colour pigments.

5 13. Use of a polymer composition according to any of claims 1 to 10 for the manufacture of polymer articles by injection moulding or compression moulding, thermoforming, blow moulding, film or sheet extrusion, pipe or cable extrusion.

14. The use of claim 13, wherein caps and closures for food, household, hygiene and health-care applications are manufactured.

# INTERNATIONAL SEARCH REPORT

Interr. Application No

PCT/EP 98/07215

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08K5/00 C08L23/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 369 658 A (SUMITOMO) 23 May 1990 see page 2, line 40 - line 45; claims 1-3; examples; table 1 ---	1,4,5
A	EP 0 417 319 A (MITSUBISHI) 20 March 1991 cited in the application see page 2, line 24 - line 35; claims 1,5; examples ---	1,4-7
A	GB 1 104 665 A (ICI LTD.) see page 1, line 19 - line 20 see page 1, line 39 - line 53 see page 1, line 65 - line 70 see page 2, line 24 - line 26 see page 3, line 52 - line 61; claims 1,4,5,11,13,19,34; examples --- -/--	1,4-6,13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

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PCT/EP 98/07215

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 151 883 A (SUMITOMO) 21 August 1985  cited in the application  see page 15, line 23 - page 16, line 2;  claims 1,6-9; examples; table 2  -----</p>	1,4-6

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Information on patent family members

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